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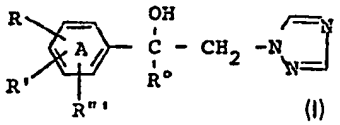
(54) α-Amyl-1H-1,2,4-triazole-1-ethanols

(57) Compounds of the formula



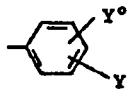
(I)

wherein

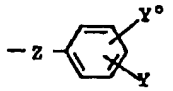
R° is $C_{1\text{ to }12}$ alkyl, $C_{3\text{ to }8}$ cycloalkyl or $C_{4\text{ to }11}$ cycloalkylalkyl in which the cycloalkyl portion is of 3 to 8 carbon atoms and the alkyl portion of 1 to 3 carbon atoms, said cycloalkyl and cycloalkylalkyl groups being optionally substituted by one or $C_{1\text{ to }3}$ two alkyl groups,

R is hydrogen, F, Cl or Br, $C_{1\text{ to }4}$ alkyl, mono-, di or tri-halo-$C_{1\text{ to }4}$ alkyl in which the halo is F, Cl, or Br, $C_{1\text{ to }4}$ alkoxy, $C_{1\text{ to }4}$ alkylthio or nitro, and

R′ is hydrogen, F, Cl, Br or I, $C_{1\text{ to }4}$ alkyl, mono-, di or tri-halo-$C_{1\text{ to }4}$ alkyl in which the halo is F, Cl or Br, $C_{1\text{ to }4}$ alkoxy, mono-, di- or tri-halo-$C_{1\text{ to }4}$ alkoxy in which the halo is F, Cl or Br, $C_{1\text{ to }4}$ alkylthio, nitro, —CN, —COOR″,



or



R″ is hydrogen, $C_{1\text{ to }4}$ alkyl,

R‴ is hydrogen, F or Cl or C_{1-2} alkyl,

Z is oxygen or sulfur, or

R and R′ together represent alkylenedioxy of 1 or 2 carbon atoms substituted onto adjacent carbon atoms of the phenyl Ring A, and

Y° and Y are independently hydrogen, F, Cl or Br, $C_{1\text{ to }4}$ alkyl or $C_{1\text{ to }4}$ alkoxy,

their preparation and their use as agricultural fungicides.

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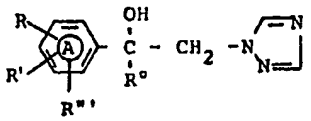
SPECIFICATION

Improvements In Or Relating to Organic Compounds

The present invention relates to α-aryl-1H-1,2,4-triazole-1-ethanols, more particularly α-alkyl-α-phenyl-1H-1,2,4-triazole-1-ethanols, their use as fungicides and agricultural compositions for facilitating such use.

More specifically, the present invention provides compounds of formula I,

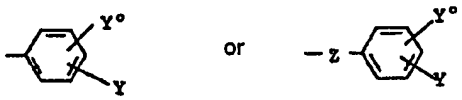


I

wherein R° is alkyl of 1 to 12 carbon atoms, cycloalkyl of 3 to 8 carbon atoms or cyclo-alkylalkyl of 4 to 11 carbon atoms in which the cycloalkyl portion is of 3 to 8 carbon atoms and the alkyl portion of 1 to 3 carbon atoms, said cycloalkyl and cycloalkylalkyl groups being optionally substituted by one or two alkyl groups of 1 to 3 carbon atoms,

R is hydrogen, halogen having an atomic number of from 9 to 35, alkyl of 1 to 4 carbon atoms, mono-, di- or tri-haloalkyl of 1 to 4 carbon atoms in which the halo is independently an halogen having an atomic number of from 9 to 35, alkoxy of 1 to 4 carbon atoms, alkylthio of 1 to 4 carbon atoms, or nitro, and

R′ is hydrogen, halogen having an atomic number of from 9 to 53, alkyl of 1 to 4 carbon atoms, mono-, di- or tri-haloalkyl of 1 to 4 carbon atoms in which the halo is independently an halogen having an atomic number of from 9 to 35, alkoxy of 1 to 4 carbon atoms, mono-, di or tri-haloalkoxy of 1 to 4 carbon atoms in which the halo is independently an halogen having an atomic number of from 9 to 35, alkylthio of 1 to 4 carbon atoms, nitro, —CN, —COOR″,



R″ is hydrogen, alkyl of 1 to 4 carbon atoms,

R‴ is hydrogen, an halogen having an atomic number of from 9 to 17 or alkyl or 1 or 2 carbon atoms,

Z is oxygen or sulfur, or

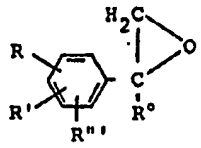
R and R′ together represent alkylenedioxy of 1 to 2 carbon atoms substituted onto adjacent carbon atoms of the phenyl Ring A, and

Y° and Y are independently hydrogen, halogen having an atomic number of from 9 to 35, alkyl of 1 to 4 carbon atoms or alkoxy of 1 to 4 carbon atoms.

Halogen atoms having an atomic number of from 9 to 53 are fluoro, chloro, bromo and iodo, such having an atomic number of from 9 to 35 are fluoro, chloro, bromo and those having an atomic number of from 9 to 17 are fluoro and chloro.

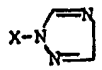
When any R or R′ is or includes mono-, di- or tri-haloalkyl this is e.g. CF_3.

The invention also provides processes for the production of compounds of formula I comprising a) reacting a compound of the formula II:



II

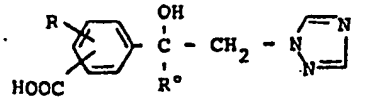
wherein R°, R, R′ and R‴ are as above defined, with a compound of formula III



III

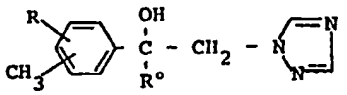
wherein X is an alkali metal in an inert organic solvent,

b) obtaining a compound of formula Ia,



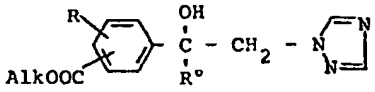
Ia

wherein R° and R are as defined above by oxidation of the CH_3 group of a compound of formula Ib,



Ib

wherein R° and R are as defined above, or c) obtaining a compound of formula Ic,



Ic

wherein R and R° are as defined above and

Alk is C_{1-4}alkyl,

by esterification of a compound of formula Ia with an alcohol of formula IV

Alk—OH IV

wherein Alk is as defined above, or a reactive functional derivative thereof.

The process a) may be carried out at temperatures typically from 0°C to 180°, preferably 40°C to 120°C, in an inert organic solvent of conventional type, e.g. an amide of an organic carboxylic acid such as dimethylformamide. As is conventional, the compound of the formula III is preferably provided by reacting triazole with a strong base such as an alkali metal hydride e.g. sodium hydride, in an inert organic solvent which is conveniently the same solvent which is to be used in process a).

The oxidation according to process b) may be carried out with the aid of oxidizing agent capable of oxidizing an CH_3-group to a COOH group. Suitable oxidizing agents are potassium permanganate, manganese dioxide and the like, preferably potassium permanganate. The reaction is conveniently carried out in aqueous solution. A suitable reaction temperature for process b) is from 20° to 150°C, preferably from 60° to 120°C.

The compounds of formula Ia are depending on the reaction conditions and the recovery steps obtained in free form or in salt form (H or COOH substituted by a cation). Free forms of compounds of formula Ia may be converted into salt forms in conventional manner and vice versa. The cation of the salt form of compounds of formula Ia is preferably an agriculturally acceptable cation such as N^+, K^+ and NH_4^+.

The process c) may be carried out in accordance with known esterification procedures for compounds containing a potentially reactive hydroxyl group. The esterification with an alcohol of formula IV is conveniently carried out at a reaction temperature of from 30°C to 80°C, advantageously under anhydrous conditions and in the presence of an acid, such as hydrogen chloride. Suitable solvents for this reaction are inert organic solvents or an excess of the alcohol of formula IV. Suitable reactive functional derivatives of an alcohol of formula IV are the corresponding diazoalkane, e.g. a diazoalkane of 1 to 3 carbon atoms, or an alkylhalide, particularly a chloride, bromide or iodide. The reaction with a diazoalkane is conveniently carried out under anhydrous conditions in an inert organic solvent. A suitable reaction temperature is then −20°C to +40°C, more usually −5°C to +20°C. For the reaction with an alkylhalide the compounds of formula Ia are preferably in salt form, e.g. the alkali metal and silver salt form. Such reaction is conveniently carried out in an inert organic solvent at temperatures of from 0°C to 100°C, more usually 40°C to 90°C.

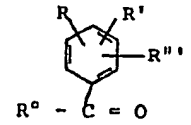
The reaction product of processes a), b) and c) may be recovered from the reaction mixture in which it is formed by working up by established procedures.

The compounds of formula I wherein R' is other than COOH may be prepared and used in the form of acid addition salt forms. The compounds of formula I are ethanol derivatives and can therefore exist in free form and in alternate forms such as an ethanolate salt form, e.g. a sodium enthanolate form, and in metal complex form, e.g. of metals from the groups Ib, IIa, IIb, VIb, VIIb and VIII of the periodic table, such as copper and zinc, and with anions such as chloride, sulphate, nitrate, carbonate, acetate, citrate, dimethyldithiocarbamate and the like.

Any salt form of compounds of formula I is preferably in the form of an agriculturally acceptable salt form.

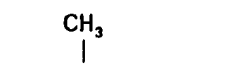
The acid addition salt forms, the ethanolate salt form and the metal complex form can be prepared from the corresponding free form in conventional manner and vice versa.

The compounds of formula II may be prepared by reacting a compound of the formula V



V

wherein R°, R, R' and R''' are as above defined, with the reaction product of a strong base and trimethylsulfonium iodide which provides a reagent which may be represented by the formula VI



VI

which process is carried out in an inert organic solvent. This process is a known type reaction for the preparation of epoxy derivatives from ketones.

Many of the compounds of the formula V are known and those which are not known *per se* may be prepared from known materials by procedures analogous to those known for preparation of the known compounds. Many of the compounds II are also known.

The compounds of the formula I are useful as fungicides in combatting phytophathogenic fungi, including particularly powdery mildews and rust fungi, as indicated by standard *In vivo* and *in vitro* tests of the type hereinafter illustrated. For such use the compounds of the formula I may be applied to plants, seed or soil in a manner conventional in the use of fungicidal agents. As will be appreciated, the amount of the compound of the formula I to be applied will vary depending upon known factors such as the particular compound employed, whether the treatment is prophylactic or therapeutic, whether the compound is applied as a foliar spray, a soil treatment or a seed dressing, the species of fungus under treatment and the time of application. However, in general, satisfactory results are obtained when the compound is applied to a crop locus, either on crops or to soil, at a rate of from about 0.005 to 2, preferably about 0.01 to 1 kg (active ingredient)/hectare. The treatment may be repeated as required, e.g. at 8 to 30 day intervals. When employed as a seed dressing, satisfactory results are obtained when the compound is employed at a rate of from about 0.05 to 0.5, preferably about 0.1 to 0.3 g/kg seed.

The term "soil" as used herein is intended to embrace any conventional growing medium whether natural or artificial.

The invention also provides, as an additional feature, fungicidal compositions, comprising, as fungicide, a compound of formula I in free form or in agriculturally acceptable salt form and an inert fungicide carrier or diluent. In general, such compositions, contain from about 0.0005 to 90, preferably from about 0.1 to 60% by weight of active agent. They may be in concentrate form, for dilution down prior to application, or in dilute, ready to apply, form. As examples of particular forms may be given wettable powder, emulsion concentrate, dusting, spraying, granulate and delayed release forms, incorporating conventional carriers and such other diluents and/or adjuvants acceptable in the agricultural art. Application forms of those compositions generally contain between about 0.0005 and 10% by weight of a compound of formula I as active agent. Typical spray suspensions may contain, for example, from 0.0005% to 0.05%, preferably 0.001% to 0.02% by weight of active ingredient. Concentrate forms of compositions for fungicide use generally contain between about 2 and 90%, preferably between about 5 and 70%, by weight of a compound of formula I as active agent. Emulsion concentrate forms generally contain from about 10 to 70%, preferably about 20 to 60% by weight of active ingredient. Solid, particulate compositions are preferred.

The compositions particularly adapted for spraying preferably include a surfactant such as a liquid polyglycol ether, a fatty alkyl sulphate or a lignin sulphonate.

In addition to conventional carrier and surface-active materials, formulations of the compound I of the invention may also contain further additives with special purposes e.g. stabilizers, deactivators (for solid formulations on carriers with an active surface), agents for improving the adhesion to plants, corrosion inhibitors, anti-foaming agents and colorants.

Moreover, further fungicides, bactericides or other beneficially-acting materials, such as insecticides, may be present in the formulations and are contemplated as further embodiments of this invention.

Examples of the production of fungicide formulations are as follows:

a) Wettable Powder Formulation

50 parts of a compound of formula I, e.g. α-t-butyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol are ground with 2 parts of lauryl sulphate, 3 parts sodium lignin sulphonate and 45 parts of finely divided kaolinite until the mean particle size is below 5 microns. The resulting spray liquor may be applied by foliar spray as well as by root drench application.

b) Granulate Formulation

Onto 94.5 parts by weight of quartz sand in a tumbler mixer is sprayed 0.5 parts by weight of a binder (non-ionic tenside) and the whole thoroughly mixed. 5 Parts by weight of a compound of formula I, e.g. powdered α-t-butyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol are then added and thorough mixing continued to obtain a granulate formulation with a particle size in the range of from 0.3 to 0.7 mm. The granulate may be applied by incorporation into the soil adjacent the plants to be treated.

c) Emulsion Concentrate

25 Parts by weight of a compound of formula I, e.g. α-t-butyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol are mixed with 30 parts by weight of iso-octyl phenyl octaglycol ether and 45 parts by weight of a petroleum fraction with a boiling range of 210—280°C (D_{20}:0.92). The concentrate is diluted with water to the desired concentration.

d) Seed Dressing

45 Parts of a compound of a compound of formula I, e.g. α-t-butyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol are mixed with 1.5 parts of diamyl phenoldecaglycolether ethylene oxide adduct, 2 parts of spindle oil, 51 parts of fine talcum and 0.5 parts of colorant rhodamin B. The mixture is ground in a contraplex mill at 10,000 rpm until an average particle of less than 20 microns is obtained. The resulting dry seed dressing powder has good adherance and may be applied to seeds, e.g. by mixing for 2 to 5 minutes in a slowly turning vessel.

Fungi against which the compounds of the formula I are indicated to be particularly of interest include by way of illustration the following:

A) *Basidiomycetes,* comprising

A.1) those of the Order *Uredinales* such as those of the genus *Uromyces* in plants such as beans, e.g. *Uromyces appendiculatus,* and ornamentals, e.g. *Uromyces dianthi,* those of the genus *Hemileia* in plants such as coffee, e.g. *Hemileia vastatrix,* those of the genus *Puccinia* in plants such as cereals (e.g. wheat, oats, barley) e.g. *Puccinia graminis, Puccinia recondita* and *Puccinia striiformis,* or ornamentals, e.g. *Puccinia pelargonii-zonalis* and *Pucc. antirrhini,* those of the genus *Phakopsora* in plants such as soya, e.g. *Phakopsora pachyrhizi,* those of the genus *Melampsora* in plants such flax, e.g. *Melampsora lini,* and those of the genus *Tranzschelia,* e.g. *Tranzschelia pruni* in plums;

A.2) those of the Order *Ustilaginales* such as those of the genus *Ustilago* in plants such as barley, wheat, corn and sugarcane, e.g. *U. maydis* on corn and *U. nuda* on barley, and

A.3) those of the genus *Stereum* in pip and stone fruit trees, e.g. *Stereum purpureum* in apple and prune.

B) *Ascomycetes,* comprising

B. 1) those of the Order *Erysiphales* such as those of the genus *Erysiphe* in plants such as cucumber, barley, wheat and sugarbeet, e.g. *Erysiphe graminis f. sp. tritici* on wheat and *Erysiphe cichoraceareum* on cucumbers; those of the genus *Spohaerotheca* on cucumbers and roses, e.g. *Spohaerotheca pannosa* on roses; those of the genus *Podosphaera* in apples, pears and prunes, e.g. *Podosphaera leucotricha* on apples; those of the genus *Uncinula* on plants such as grapes, e.g. *Uncinula necator* on grapevines; those of the "genus" *Oidium* on a wide variety of plants; and those of the genus *Leveillula* in plants such as cotton and other *Malvaceae,* e.g. *Leveillula taurica* on cotton.

C) *Oomycetes,* comprising

C.1) those of the genus *Phytophthora spp.,* e.g. *Ph. cactorum, Ph. parasitica* and *Ph. cinamomi* on susceptible plants; and

C.2) those of the genus *Aphanomyces* in plants such as pea and sugar beet, e.g. *Aphanomyces euteiches* in sugar beet, and

D) *Deuteromycetes,* comprising

D.1) those of the genus *Helminthosporium* in plants such as barley and corn, e.g. *Helm. Sativum;*

D.2) those of the genus *Septoria* in plants such as wheat, tomato and celery, e.g. *Sept. tritici* in wheat, tomato and celery, e.g. *Sept. tritici* in wheat;

D.3) those of the genus *Rhizoctonia* in plants such as cotton and potato, e.g. *Rhiz. solani* in cotton;

D.4) those of the genus *Fusarium spp,* e.g. *F. oxysporum f. sp. lycopersici* in tomato, *F. oxysporum f. sp. vasinfectum* in cotton, *F. oxysporum f. sp. cubense* in banana, *F. solani* in vegetables, *F. culmorum* in cereals and *F. graminearum* in cereals;

D.5) those of the genus *Thielaviopsis* in plants such as cotton, tobacco etc., e.g. *Thielaviopsis basicola* in cotton;

D.6) those of the genus *Phoma* in plants such as sugar beet, rape etc., e.g. *Phoma betae* in sugar beet;

D.7) those of the genus *Piricularia spp.,* e.g. *P.oryzae* on rice; and

D.8) those of the genus *Colletotrichum spp.,* e.g. *C. lindemuthianum* in beans.

The following conventional tests are illustrative of the manner by which the fungicidal activity of the compounds of the formula I may be indicated.

Test Method A: In vivo employing bean rust *(Uromyces appendiculatus). Phaseolus vulgaris* (pole bean plant) is cultivated in a mixture of peat and sand in plastic pots of 6 cm diameter for 9 days. The plants are sprayed with a spray liquor containing 0.0008 to 0.05% (e.g. at 0.00008%, 0.003%, 0.012% and 0.05%) active ingredient. Treatment comprises foliar spraying to near run-off or soil drenching (28 ml of spray liquor per pot). After drying, the plants are inoculated with a spore suspension spray (500,000 to 700,000 spores/ml) and incubated for 7 days in an incubation chamber at 100% relative humudity and 21°. The efficacy of the active agent treatment is determined by comparing the number

of pustules/leaf with that on untreated, similarly inoculated check plants. The compounds of formula I, particularly the compounds of the Examples hereinafter e.g. the compounds of the Examples 1, 1A, 1B, 1C, 2A, 2B, 2D, 2F, 2G, 2H, 2L, 2N, 2P, 2Z-1, 2Z-3, 2Z-4, 2Z-7, 2Z-8, 2Z-9, 2Z-11, 2Z-13, 2Z-14, 2Z-15, 2Z-24, 2Z-27, 2Z-28, 2Z-32, 2Z-33, 2Z-41, to 2Z-44 and 3 hereinafter used in the wettable powder formulation given above provide a significant degree of fungicidal activity in the above test, both by contact as well as root-systemic action.

Analogous tests are run on the following crop/fungi with similar results.

Coffee: coffee leaf rust *(hemileia vastatrix)*

Wheat: black stem rust *(Puccinia graminis)*

Wheat: brown leaf rust *(Puccinia recondita)*

Wheat: yellow or stripe rust *(Puccinia striiformis)*

Flax: flax rust *(Melamspora Lini)*

Pelargonium: Pelargonium rust *(Puccinia pelargoniizonalis)*

Snapdragon: Snapdragon rust *(Puccinia antirrhini)*.

Test Method B: In vivo employing cucumber powdery mildew *(Erysiphe cichoracearum). Cucumis sativus* (cucumber) is cultivated in a mixture of peat and sand in plastic pots of 6 cm diameter for 7 days. The plants are sprayed with a spray liquor containing 0.0008 to 0.05% (e.g. at 0.0008%, 0.003%, 0.012% and 0.05%) active ingredient. Treatment comprises foliar spraying to near run-off or soil drenching (28 ml of spray liquor per pot). After drying, the plants are inoculated by dusting them with freshly collected *conidia* and are then incubated for 7 days in an incubation chamber at 60—80% relative humidity and 25—30°C.The efficacy of the active ingredient is determined by comparing the degree of fungal attack with that on untreated, similarly inoculated check plants. The compounds of formula I, particularly the compounds of the examples hereinafter, e.g. the compounds of the Examples 1, 2A, 2B, 2C, 2D, 2F, 2G, 2H, 2L, 2N, 2P, 2Q, 2R, 2S, 2T, 2U, 2V, 2Z-1, 2Z-3, 2Z-4, 2Z-6 to 2Z-9, 2Z-11, 2Z-13 to 2Z-15, 2Z-24, 2Z-26, 2Z-27, 2Z-28, 2Z-35, 2Z-40 to 2Z-47, 1A, 1B, 1C and Example 3 hereinafter used in the wettable powder formulation given above provide a significant degree of fungicidal activity, both by contact as well as root-systemic action.

Test analogous to Test Method B are made with similar results on the following crop/fungi:

Wheat: wheat powdery mildew *(Erys. gram, f.sp. tritici)*

Barley: barley powdery mildew *(Erys. gram. f.sp. hordei)*

Apple: apple powdery mildew *(Podos. leucotricha)*

Grape; grapevine powdery mildew *(Uncinula necator)*

Test Method B, above, as regards cucumber powdery mildew and the preferred compound of Example 1, hereinafter is repeated (both foliar spray and soil drench) but at the lower concentrations of 0.0002% and 0.00005% with the result that 100% control of the fungi is still obtained, thereby still further indicating the remarkable potency provided by the invention. At concentrations of 0.000012% and 0.000003% in the same test a control of 70% and 50%, respectively, is obtained in spray application and a control of 90% and 70%, respectively in the soil drench application. In repeating Test Method B, above, against barley powdery mildew at the 0.0002% and 0.00005% concentrations a control of 70% and 55%, respectively, is obtained on spray application and a control of 80% and 70%, respectively, is obtained in soil drench application. Against wheat powdery mildew in the Test Method B at the 0.0002% and 0.00005% concentrations a control of 80% and 60%, respectively, is obtained on spray application and a control 90% and 70%, respectively, in the soil drench application.

Test Method C; *In vitro* test employing *Ustilago maydis (corn smut).* Different concentrations of the active ingredient are incorporated in malt agar plates to give concentrations of 0.8 to 200 ppm a.i. (e.g. at 0.8, 3.2, 12.5, 50 and 200 ppm). The plates are then inoculated by spraying a spore suspension of *U. maydis* onto them or placing an agar plug containing the fungis in the centre of the plate. The plates are incubated at room temperature for 2—5 days. The efficacy of the active agent treatment is determined by comparing the growth of the fungus with that in untreated, similarly inoculated plates. The compounds of formula I provide moderate to good control in test Method C. The compounds of Example 1, 2A, and 2Z-1 hereinafter provide for example good control at both the lower and higher concentrations in Test Method C. In an analogous test on *Fusarium oxysporum f.sp.* the compounds of formula I, e.g. the compounds of Example 2A, 2B, 2D, 2P, 2R, 2S, 2Z, 2Z-32, 2Z-34 and 2Z-46 hereinafter provide moderate to good control.

Fungi of the aforementioned genera cause considerable damage in agriculture and are difficult to prevent or control. In addition to combatting such fungi, the compounds of the formula I are indicated to be non-phytotoxic at effective doses in plants subject to such fungi and are further indicated to be of particular interest as also acting to combat fungi by systemic action as determined, for example, in the combatting of *Uromyces appendiculatus* on beans.

Additional tests analogous to Test Method C at 13, 50 and 200 ppm a.i. show, except where indicated, a 100% control with the compound of Example 1 hereinafter at at least one test dosage on the following: *Phytophthora cactorum* (maximum control 45%); *Phytophthora cinamomi* (maximum control 65%); *Aphanomyces euteiches; Stereum purpureum; Thielaviopsis basicola; Piricularia oryzae;* and *Colletotrichum lindemuthianum* (maximum control 90%).

Additional tests analogous to Test Methods A and B at doses of 32, 125 and 500 ppm a.i.

conducted with the compound of Example 1 hereinafter show by spray application a 75%, 95% and 100% control, respectively of *Helminthosporium* on barley with 20% phytotoxicity at the higher dose.

Test Method D: In vivo, employing *Rhizoctonia solani.* The fungus is cultivated in a sterile mixture of Zonolite and corn meal (10:1 w/w) to which water is added in a ratio of about 1:1 (w/w); cultivation lasts for 14 days at 25°C. The fungus is then mixed into a semi-sterile mixture of peat and sand which then is treated with a suspension containing the formulated active ingredient to give concentration of 10 to 160 ppm (e.g. 10, 40 and 160 ppm) calculated per volume substrate. The substrate is transferred to pots of 5 cm diameter which are planted with cotton seedlings (cotyledonous stage). The planted pots are inoculated at 24°C and 60—70% relative humidity in an incubation chamber for 14 days, after which disease attack is determined by comparing the fungal attack on roots and hypocotyl with that on untreated, similarly inoculated check plants. The compounds of formula I provide good control in test D. The compound of Example 1, hereinafter, used in the wettable powder formulation given above, provides for example 100% disease control with no phytotoxicity at the lower dose.

In a test analogous to Test Method D run with *Phoma betae* on sugar beet, the compound of formula I, e.g. the compounds of formula 1, 1A, 1B, 1C, 2A, 2B, 2D, 2N, 2P, 2R, 2Y, 2Z, 2Z-1, 2Z-4, 2Z-7, 2Z-8, 2Z-11, 2Z-15, 2Z-32, 2Z-33, 2Z-34 and 2Z-41 provide good control.

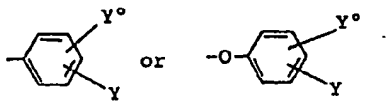
From the foregoing it will be evident to those skilled in the art that the compounds of the present invention are also indicated to be of particular interest with regard to the control of important soil- and seed-borne fungi, e.g. *Helminthosporium, Phoma, Rhizoctonia* and *Thielaviopsis,* in addition to their considerable interest and value in the control of powdery mildews and rusts.

The particular value and advantages of the invention are confirmed and/or further indicated in more detailed evaluations of the compound of Example 1 hereinafter which exhibits the following outstanding and in some cases remarkable properties: 1) a persistency of action that still produces 100% control of *Uromyces app.* on pole beans at spray concentrations of 0.012% on application 8 days before inoculation; 2) a good stability of aqueous spray suspensions as indicated by 100% control of *Uromyces app.* on pole beans on application 3 days after preparation of the suspension (0.012% concentration); 3) rapid and lasting penetration of the active substance into leaves of plants to be protected as indicated by 100% control at the 0.012% concentration after a) washing the leaves of pole beans for 10 minutes only 10 minutes after application of the active ingredient followed by infestation with *Uromyces app.,* b) washing the leaves of grapevine for 15 minutes 2 hours after application of the active ingredient followed by infestation with *Uncinula,* c) simulated rain washing of the leaves of coffee plants at a rain rate of 50 MM/hour first applied two hours after application of the active ingredient for 15 minutes followed by drying, a second application of rain for 15 minutes again followed by drying and then a third application of rain for 15 minutes, followed by infestation of the coffee plant with *Hemileia vastatrix,* and d) simulated rain washing of the leaves of pole beans at a rain rate of 50 MM/hour first applied 2 hours after application of the active ingredient for 10 minutes followed by drying, a second application of rain for 10 minutes again followed by drying and then a third application of rain for 10 minutes, followed by infestation of pole bean plants with *Uromyces app;* and 4) outstanding systemicity of action involving transport after uptake through the leaves of the upper or lower portions of grapevine to the other portion which is untreated whereby a 70% and 75% control of *Uncinula* in the untreated upper and lower leaves, respectively, is observed, indicating that such transport into the untreated leaves takes place both acro- and basipetally. In still further evaluation of the compound of Example 1 hereinafter a fungicidal activity of 100% compared with untreated standard is obtained on application of the active ingredient at a concentration of 0.012% 3 days (before sporulation) after pole beans are infested with *Uromyces app.*

When applied at a concentration of 0.05% onto pole bean plants already showing sporulation pustules of *Uromyces app.* there is obtained a 60% control of visible disease symptoms compared to an untreated control 10 days after application with a 50% control obtained after only 3 days after application. From the foregoing further evaluations of the compound of Example 1 the desired properties of a curative activity and at least a partial eradicative effect are indicated.

Other compounds of the formula I particularly the compounds of Examples 2A, 2B, 2D, 2F, 2G, 2H, 2L, 2N, 2P, 2Z-1, 2Z-3, 2Z-4, 2Z-7 to 2Z-9, 2Z-11, 2Z-13 to 2Z-15, 2Z-24, 2Z-32, 2Z-33, 2Z-43 to 2Z-45 and 3 hereinafter also show very good to outstanding fungicidal activity in evaluation procedures described above. The fungicidal activity of the compound of Example 2A is for example at least equal to the activity of the compound of Example 1 and also the compound of Example 2Z-33 has the same order of fungicidal activity as that of Example 1.

Preferred compounds of the formula I have one or more and preferably all of the following features: a) R^o is alkyl of 2 to 10 carbon atoms, particularly alkyl of 3 to 10 carbon atoms and more particularly alkyl of 3 to 6 carbon atoms, cycloalkyl of 3 to 6 carbon atoms or cycloalkylmethyl in which the cycloalkyl portion is of 3 to 6; b) R is hydrogen, fluoro, chlor, bromo, CF_3 or C_1—C_4 alkyl; c) R′ is hydrogen, fluoro, chloro, bromo, C_1—C_4 alkyl, C_1—C_4 alkoxy, alkylthio of 1 to 4 carbon atoms, CN,



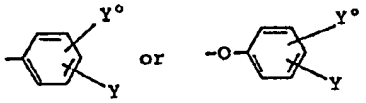
wherein Y° and Y are as above defined; d) R''' is hydrogen. The more preferred among the above-mentioned preferred compounds of the formula I have one or more and preferably all of the following features:

a) R° is alkyl of 3 to 6 carbon atoms or cycloalkyl of 3 to 6 carbon atoms such as cyclopropyl and cyclopentyl;

b) R is hydrogen, fluoro, Cl, Br, CF_3 or C_1—C_2 alkyl; and

c) R' is hydrogen, fluoro, Cl, CN, C_1—C_2 alkyl or C_1—C_2-alkoxy; or

d) R is hydrogen and R' is



located at the para-position of Ring A, more preferably with Y° and Y being hydrogen.

The particularly preferred compounds of the formula I are indicated to be those in which R° is propyl or butyl, e.g. n-propyl, isopropyl, n-butyl, sec.-butyl, i-butyl and t-butyl, especially n-propyl, isopropyl, the branched butyls and most especially t-butyl. Other branched alkyls of 5 to 6 carbon atoms, e.g. isopentyl and neopentyl, are also indicated to be particular interest. Also of particular interest are those in which R° is cyclopropyl, cyclopentyl or cyclohexyl.

The following examples further illustrate the present invention. All temperatures are in centigrade.

Example 1

α-t-butyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol

A 0.62 g portion of 61.4% sodium hydride is washed three times with petroleum ether and then 10 ml of dimethylformamide is added while maintaining stirring. To the resulting suspension is added slowly with stirring 1.1 g of triazole in 10 ml of dimethylformamide followed by stirring at 20° until bubbling ceases. To the resulting mixture is then added 3.0 g of 2-(2-butyl)-2-(4-methylphenyl)-oxirane followed by heating with stirring at 90° for 6 hours. The resulting reaction mixture is then poured onto water, extracted with ethyl acetate, dried and chromatographed over silica gel while eluding with hexane/chloroform (50:50) to obtain a yellow oil which crystallizes on standing to a solid which on recrystallization from ethanol yields α-t-butyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 69—71°. The corresponding hydrogen oxalate (Example 1A) has a m.p. of 147—150°, the p-methylbenzene sulfonate Example 1B) a m.p. of 215—220° and the hydrochloride (Example 1C) a m.p. of 247—250°, and the sodium ethanolate of the title compound a m.p. of >250° (Example 1D).

Example 2

Following the procedure of Example 1 the following additional compounds of the invention are obtained:

A) α-t-butyl-α-(p-chlorophenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 114—115°.
B) α-t-butyl-α-(o,p-dichlorophenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 63—64°.
C) α-t-butyl-α-(m,p-dichlorophenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 156—157°.
D) α-t-butyl-α-phenyl-1H-1,2,4-triazole-1-ethanol, m.p. 84—86°.
E) α-n-decyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol.
F) α-t-butyl-α-(p-fluorophenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 104—106°.
G) α-t-butyl-α-(p-methoxyphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 76—79°.
H) α-n-butyl-α-(o,p-dichlorophenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 109—110°.
I) α-n-propyl-α-(p-chlorophenyl)-1H-1,2,4-triazole-1-ethanol.
J) α-i-butyl-α-(p-chlorophenyl)-1H-1,2,4-triazole-1-ethanol.
K) α-methyl-α-(p-chlorophenyl)-1H-1,2,4-triazole-1-ethanol.
L) α-t-butyl-α-(p-biphenylyl)-1H-1,2,4-triazole-1-ethanol, m.p. 117—118°.
M) α-t-butyl-α-(m,p-methylene dioxyphenyl)-1H-1,2,4-triazole-1-ethanol.
N) α-t-butyl-α-(m-cyanophenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 123—124°.
O) α-t-butyl-α-(m-nitrophenyl)-1H-1,2,4-triazole-1-ethanol.
P) α-t-butyl-α-(p-phenoxyphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 112—113°.
Q) α-methyl-α-(m,p-dichlorophenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 97—99°.
R) α-n-propyl-α-phenyl-1H-1,2,4-triazole-1-ethanol, m.p. 81—83°.
S) α-ethyl-α-(p-chlorophenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 108—109°.
T) α-n-butyl-α-phenyl-1H-1,2,4-triazole-1-ethanol, m.p. 67—68°.
U) α-isopentyl-α-phenyl-1H-1,2,4-triazole-1-ethanol, m.p. 78—80°.

V) α-n-propyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 86—88°.
W) α-methyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 78—80°.
X) α-n-pentyl-α-phenyl-1H-1,2,4-triazole-1-ethanol, m.p. 89—90°.
Y) α-isopropyl-α-phenyl-1H-1,2,4-triazole-1-ethanol, m.p. 71—73°.
Z) α-n-butyl-α-(p-chlorophenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 108—109°.
Z-1) α-n-butyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 79—80°.
Z-2) α-methyl-α-(m-trifluoromethylphenyl)-1H-1,2,4-triazole-1-ethanol, as an oil.
Z-3) α-t-butyl-α-(m-trifluoromethylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 120—122°.
Z-4) α-t-butyl-α-(m-methylphenyl)-1H-1,2,4-triazole-1-ethanol. m.p. 93—94°.
Z-5) α-t-butyl-α-(o-methylphenyl)-1H-1,2,4-triazole-1-ethanol.
Z-6) α-t-butyl-α-(p-t-butylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 108—110°.
Z-7) α-t-butyl-α-(p-ethylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 91—94°.
Z-8) α-t-butyl-α-(m-phenoxyphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 133—135°.
Z-9) α-t-butyl-α-(m-methoxyphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 59—61°.
Z-10) α-t-butyl-α-(p-trifluoromethoxyphenyl)-1H-1,2,4-triazole-1-ethanol.
Z-11) α-cyclohexyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 102—103°.
Z-12) α-hexyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol.
Z-13) α-octyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 79—81°.
Z-14) α-dodecyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 78—79°.
Z-15) α-t-butyl-α-(p-bromophenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 124—125°.
Z-16) α-neopentyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol.
Z-17) α-sec.-butyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol.
Z-18) α-(1,1-dimethylpropyl)-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol.
Z-19) α-t-butyl-α-(m,m-dibromophenyl)-1H-1,2,4-triazole-1-ethanol.
Z-20) α-cyclopropyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol.
Z-21) α-(2-methylcyclopropyl)-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol.
Z-22) α-cyclohexylmethyl-α-(p.methylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 79—81°.
Z-23) α-cyclopentylmethyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 74—76°.
Z-24) α-(1-ethylpropyl)-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 87—89°.
Z-25) α-(1-methylbutyl)-α-(p-methylphenyl) -1H-1,2,4-triazole-1-ethanol.
Z-26) α-t-butyl-α-(m-bromo-p-methylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 155—158°.
Z-27) α-t-butyl-α-(m-fluoro-p-methylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 102—104°.
Z-28) α-t-butyl-α-(m-chloro-p-methylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 144—147°.
Z-29) α-t-butyl-α-(m-chloro-m-methoxyphenyl)-1H-1,2,4-triazole-1-ethanol.
Z-30) α-t-butyl-α-(p-trifluoromethyl-m-chlorophenyl)-1H-1,2,4-triazole-1-ethanol.
Z-31) α-t-butyl-α-(m-chloro-m-phenoxyphenyl)-1H-1,2,4-triazole-1-ethanol.
Z-32) α-cyclopentyl-α-phenyl-1H-1,2,4-triazole-1-ethanol, as an oil.
Z-33) α-cyclopropyl-α-(p-chlorophenyl)-1H-1,2,4-triazole-1-ethanol, as an oil.
Z-34) α-cyclobutyl-α-(p-fluorophenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 83—84°.
Z-35) α-t-butyl-α-(m,p-dimethylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 120—122°.
Z-36) α-t-butyl-α.(o-methoxy-m-methylphenyl)-1H-1,2,4-triazole-1-ethanol.
Z-37) α-t-butyl-α-(o-methyl-p-methylthiophenyl) -1H-1,2,4-triazole-1-ethanol.
Z-38) α-t-butyl-α-(m-methyl-p.phenoxyphenyl)-1H-1,2,4-triazole-1-ethanol.
Z-39) α-t-butyl-α-(o-methyl-m-nitrophenyl)-1H-1,2,4-triazole-1-ethanol.
Z-40) α-cyclobutyl-α-phenyl-1H-1,2,4-triazole-1-ethanol, as an oil.
Z-41) α-sec.-butyl-α-(p-chlorophenyl)-1H-1,2,4-triazole-1-ethanol, as an oil.
Z-42) α-t-butyl-α-(m,m'-dichlorophenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 145—147°.
Z-43) α-t-butyl-α-(m-chlorophenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 126—127°.
Z-44) α-2-butyl-α-(p-cyanophenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 105—107°.
Z-45) α-cyclopentyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol.
Z-46) α-isobutyl-α-phenyl-1H-1,2,4-triazole-1-ethanol.
Z-47) α-(1-methylcyclopropyl)-α-p.methylphenyl-1H-1,2,4-triazole-1-ethanol, m.p. 126—128°.
Z-48) α-methyl-α-(p-biphenylyl)-1H-1,2,4-triazole-1-ethanol, m.p. 115—120°.
Z-49) α-tert.butyl-α-(p-iodophenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 78—80°.
Z-50) α-(3-heptyl)-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol, oil,
Z-51) α-(2-pentyl)-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 89—91°.
Z-52) α-(tert.butyl-α-(m,m'-dimethylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 128—130°.
Z-53) α-t-butyl-α-(3-nitro-4-methylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 160—161°C.
Z-54) α-t-butyl-α-(3,5-dinitro-4-methylphenyl)-1H-1,2,4-triazole-1-ethanol, m.p. 194—196°C.

Example 3

α-t-butyl-α-(p-carboxyphenyl)-1H-1,2,4-triazole-1-ethanol, and Potassium Salt

A mixture of 1.3 g of α-t-butyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol, 1.89 g of potassium permanganate and 19 ml of water are refluxed with stirring for 1 hour. The resulting reaction mixture is filtered while still hot, the residue washed with 10 ml of hot water, the filtrate treated with

charcoal and concentrated *in vacuum* to a small volume (4 ml) which is dried under high vacuum to obtain the potassium salt of α-t-butyl-α-(p-carboxyphenyl) -1H-1,2,4-triazole-1-ethanol, m.p. 194° (decomposition).

The above reaction is repeated using three times the amounts of the materials specified above except that the filtrate is washed with ether, the ether washing washed with water, the combined aqueous layers acidified with concentrated hydrochloric acid with stirring until no additional precipitate formed, and the precipitate collected by filtration, washed several times with ether and dried under a high vacuum to obtain α-t-butyl-α-(p-carboxyphenyl) -1H-1,2,4-triazole-1-ethanol, m.p. 248—250°.

Example 4

2-(t-butyl)-2-(4-methylphenyl)-oxirane

A 2.2 g portion of 61.4% sodium hydride is washed three times with petroleum ether, then 70 ml of dimethylsulfoxide added and the mixture heated with stirring to 70° and carried to 85° by the exotherm after which the mixture is heated at 75° for 40 minutes. The resulting mixture is cooled to 0° in an ice/salt bath and then under a nitrogen blanket there is added dropwise a solution of 7.0 g of trimethylsulfonium iodide in 50 ml of dimethylsulfoxide and 20 ml. tetrahydrofuran while maintaining the temperature below 18°. To the resulting mixture is then added with stirring under the nitrogen blanket a solution of 3.0 g of t-butyl-p-methylphenyl ketone in 30 ml of tetrahydrofuran while maintaining the temperature below 10°. The resulting mixture is stirred at 0° 30 minutes and then at room temperature for 2 hours. The resulting reaction mixture is then poured onto 400 ml of water, extracted with methylene chloride, the organic phase washed with water and then brine, dried and evaporated to obtain a yellow oil of 2-(t-butyl)-2-(4-methylphenyl)-oxirane.

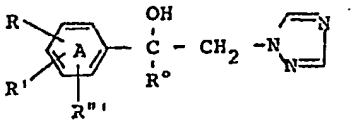
Example 5

α-(tert.-butyl)-α-(p-methoxycarbonylphenyl)-1H-1,2,4-triazole-1-ethanol

To a flask containing at 0° an ether solution of CH_2N_2 prepared in the conventional manner from 3.39 g of N-methyl-N-nitroso-p-toluenesulphonamide is added dropwise, while maintaining ice bath cooling, a solution of 1.5 g of α-(tert.-butyl)-α-(p-carboxyphenyl)-1H-1,2,4-triazole-1-ethanol in 85 ml of dry tetrahydrofuran. The resulting mixture is allowed to stand under ice cooling until thin layer chromatography analysis shows an essential absence of the triazole starting material. A few drops of acetic acid are added to destroy excess diazomethane, the mixture is then concentrated to remove tetrahydrofuran, the concentrate extracted with ether and washed with 2N NaOH solution. After drying white crystals are formed on standing. The crystals are recovered by filtering and recrystallized from CH_2Cl_2/ether to obtain the title compound, m.p. 152—154°.

Claims

1. A compound of the formula

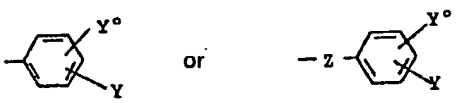


wherein

R^o is alkyl of 1 to 12 carbon atoms, cycloalkyl of 3 to 8 carbon atoms or cycloalkylalkyl of 4 to 11 carbon atoms in which the cycloalkyl portion is of 3 to 8 carbon atoms and the alkyl portion 1 to 3 carbon atoms, said cycloalkyl and cycloalkylalkyl groups being optionally substituted by one or two alkyl groups of 1 to 3 carbon atoms,

R is hydrogen, halogen having an atomic number of from 9 to 35, alkyl of 1 to 4 carbon atoms, mono-, di- or tri-haloalkyl of 1 to 4 carbon atoms in which the halo is independently an halogen having an atomic number of from 9 to 35, alkoxy of 1 to 4 carbon aroms, alkylthio of 1 to 4 carbon atoms, or nitro, and

R' is hydrogen, halogen having an atomic number of from 9 to 53, alkyl of 1 to 4 carbon atoms, mono-, di- or trihaloalkyl of 1 to 4 carbon atoms in which the halo is independently an halogen having an atomic number of from 9 to 35, alkoxy of 1 to 4 carbon atoms, mono-, di or tri-haloalkoxy of 1 to 4 carbon atoms in which the halo is independently an halogen having an atomic number of from 9 to 35, alkylthio of 1 to 4 carbon atoms, nitro, —CN, —COOR'',



R'' is hydrogen, alkyl of 1 to 4 carbon atoms,

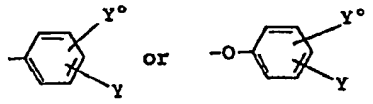
R''' is hydrogen, an halogen having an atomic number of from 9 to 17 or alkyl of 1 or 2 carbon atoms,

Z is oxygen or sulfur, or

R and R′ together represent alkylenedioxy of 1 to 2 carbon atoms substituted onto adjacent carbon atoms of the phenyl Ring A, and

Y° and Y are independently hydrogen, halogen having an atomic number of from 9 to 35, alkyl of 1 to 4 carbon atoms or alkoxy of 1 to 4 carbon atoms.

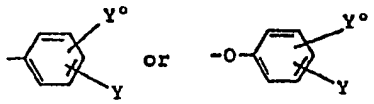
2. A compound of Claim 1 in which R is hydrogen, halogen having an atomic number of from 9 to 35, CF_3 or C_1—C_4 alkyl, R′ is hydrogen, halogen having an atomic number of from 9 to 35, C_1—C_4alkyl, C_1—C_4alkoxy, C_1—C_4alkylthio, CN,



in which Y° and Y are as defined in Claim 1, and R‴ is hydrogen.

3. A compound of Claim 2 in which R is hydrogen, F, Cl, Br, CF_3 or C_1—C_4alkyl and R′ is hydrogen, fluoro, chloro, CN, C_1—C_2alkyl or C_1—C_2alkoxy.

4. A compound of Claim 2 in which R is hydrogen and R′ is



located at the para-position of Ring A, and in which Y° and Y are as defined in Claim 1.

5. A compound of Claim 4 in which Y° and Y are each hydrogen.

6. A compound according to any one of Claims 1 to 5 in which R° is alkyl of 2 to 10 carbon atoms or cycloalkyl of 3 to 6 carbon atoms.

7. A compound of Claim 6 in which R° is alkyl of 3 to 6 carbon atoms or cycloalkyl of 3 to 6 carbon atoms.

8. A compound of Claim 7 in which R° is butyl or propyl.

9. A compound of Claim 7 in which R° is t-butyl.

10. A compound of Claim 7 in which R° is cyclopropyl.

11. A compound of Claim 7 in which R° is cyclopentyl.

12. A compound of Claim 1 which is α-t-butyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol.

13. The compound of Claim 1 which is α-t-butyl-α-(p-chlorophenyl)-1H-1,2,4-triazole-1-ethanol.

14. The compound of Claim 1 which is α-t-butyl-α-(o,p-dichlorophenyl)-1H-1,2,4-triazole-1-ethanol.

15. The compound of Claim 1 which is α-t-butyl-α-phenyl-1H-1,2,4-triazole-1-ethanol.

16. The compound of Claim 1 which is α-n-butyl-α-(o,p-dichlorophenyl)-1H-1,2,4-triazole-1-ethanol.

17. The compound of Claim 1 which is α-t-butyl-α-(p-phenoxyphenyl)-1H-1,2,4-triazole-1-ethanol.

18. The compound of Claim 1 which is α-n-butyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol.

19. The compound of Claim 1 which is α-t-butyl-α-(m-trifluoromethylphenyl)-1H-1,2,4-triazole-1-ethanol.

20. The compound of Claim 1 which is α-t-butyl-α-(m-methylphenyl)-1H-1,2,4-triazole-1-ethanol.

21. The compound of Claim 1 which is α-cyclopentyl-α-phenyl-1H-1,2,4-triazole-1-ethanol.

22. The compound of Claim 1 which is α-cyclopropyl-α-(p-chlorophenyl)-1H-1,2,4-triazole-1-ethanol.

23. The compound of Claim 1 which is α-t-butyl-α-(m,m-dichlorophenyl)-1H-1,2,4-triazole-1-ethanol.

24. The compound of Claim 1 which is α-t-butyl-α-(m-chlorophenyl)-1H-1,2,4-triazole-1-ethanol.

25. The compound of Claim 1 which is α-t-butyl-α-(p-cyanophenyl)-1H-1,2,4-triazole-1-ethanol.

26. The compound of Claim 1 which is α-cyclopentyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol.

27. The compound of Claim 1 which is α-t-butyl-α-(p-fluorophenyl)-1H-1,2,4-tralzole-1-ethanol.

28. The compound of Claim 1 which is α-t-butyl-α-(p-methoxyphenyl)-1H-1,2,4-triazole-1-ethanol.

29. The compound of Claim 1 which is α-t-butyl-α-(p-biphenylyl)-1H-1,2,4-triazole-1-ethanol.

30. The compound of Claim 1 which is α-t-butyl-α-(m-cyanophenyl)-1H-1,2,4-triazole-1-ethanol.

31. The compound of Claim 1 which is α-t-butyl-α-(p-ethylphenyl)-1H-1,2,4-triazole-1-ethanol.

32. The compound of Claim 1 which is α-t-butyl-α-(m-phenoxyphenyl)-1H-1,2,4-triazole-1-ethanol.

33. The compound of Claim 1 which is α-t-butyl-α-(m-methoxyphenyl)-1H-1,2,4-triazole-1-ethanol.

34. The compound of Claim 1 which is α-cyclohexyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol.

35. The compound of Claim 1 which is α-octyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol.

36. The compound of Claim 1 which is α-dodecyl-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol.

37. The compound of Claim 1 which is α-t-butyl-α-(p-bromophenyl)-1H-1,2,4-triazole-1-ethanol. ethanol.

38. The compound of Claim 1 which is α-(1-ethyl-propyl)-α-(p-methylphenyl)-1H-1,2,4-triazole-1-ethanol.

39. The compound according to any one of Claims 1 to 38 in free form.

40. A compound according to any one of Claims 1 to 38 in salt form or metal complex form.

41. The method of combatting phytopathogenic fungus in plants, seeds or soil comprising treating said plants, seeds or soil with a non-phytotoxic fungicidally effective amount of a compound claimed in any one of Claims 1 to 40 in free form or in an agriculturally acceptable salt or metal complex form.

42. The method of combatting phytopathogenic fungus in plants or soil comprising applying to said plants or soil 0.005 to 2 kg per hectare of a compound claimed in any one of Claims 1 to 40.

43. The method of Claim 42, wherein the application rate is from 0.01 to 1 kg per hectare of a compound claimed in any one of Claims 1 to 40.

44. The method of combatting phytopathogenic fungus in seeds comprising applying to the seeds 0.05 to 0.5 g per kg seed of a compound claimed in any one of Claims 1 to 40.

45. The method of Claims 44, wherein the application rate is from 0.1 to 0.3 g per kg seed of a compound claimed in any one of Claims 1 to 40.

46. A fungicidal composition comprising a compound claimed in any one of Claims 1 to 40 in free form or in agriculturally acceptable salt or metal complex form in association with a fungicide carrier or diluent.

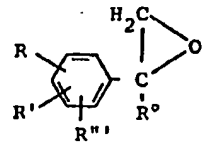
47. The composition of Claim 46, comprising from 0.0005 to 90% by weight of a compound claimed in any one of Claims 1 to 40 in free form or in agriculturally acceptable salt or metal complex form.

48. An application form of the composition of Claim 47, comprising from 0.0005 to 10% by weight of a compound claimed in any one of Claims 1 to 40 in free form or in agriculturally acceptable salt or metal complex form.

49. A concentrate form of the composition of Claim 47, comprising from 2 to 80% by weight of a compound claimed in any one of Claims 1 to 40 in free form or in agriculturally acceptable salt or metal complex form.

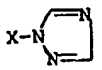
50. A process for the production of compounds of formula I, stated in Claim 1, which comprises

a) reacting a compound of the formula II:



II

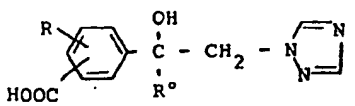
wherein R°, R, R' and R''' are as above defined, with a compound of formula III



III

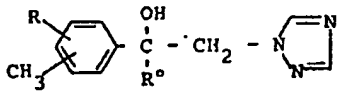
wherein X is an alkali metal in an inert organic solvent,

b) obtaining a compound of formula Ia,



Ia

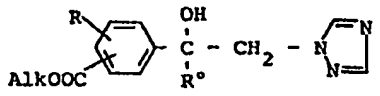
wherein R° and R are as defined above by oxidation of the CH_3 group of a compound of formula Ib,



Ib

wherein R° and R are as defined above, or

c) obtaining a compound of formula Ic,



Ic

wherein R and R° are as defined above and

Alk is C_{1-4}alkyl,

by esterification of a compound of formula Ia with an alcohol of formula IV

Alk—OH IV

wherein Alk is as defined above, or a reactive functional derivative thereof.

51. A process according to Claim 50, substantially as hereinbefore described with reference to any one of the Examples.

52. A compound of formula I, stated in Claim 1, whenever obtained by a process according to Claim 50 or 51.

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